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(72) SCHWOB, YVAN, FR

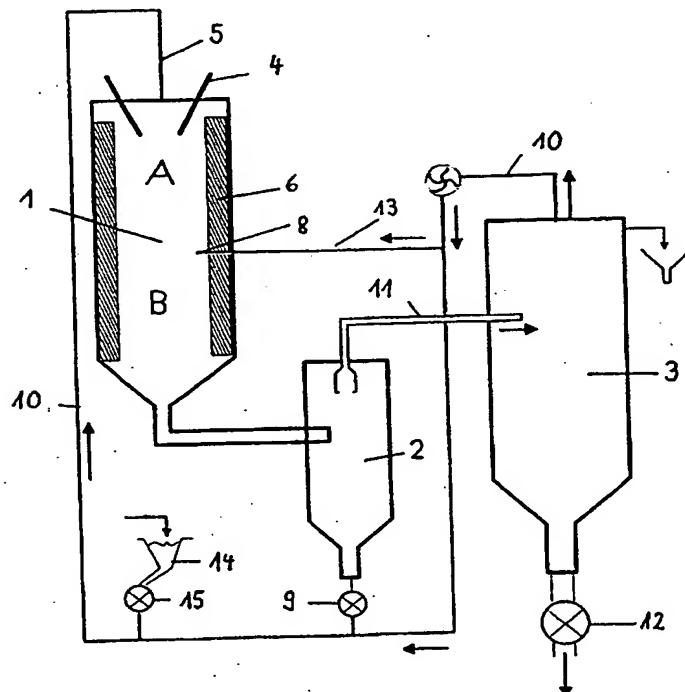
(71) SCHWOB, YVAN, FR

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(54) **PROCEDE ET DISPOSITIF POUR LA FABRICATION DE
FULLERENES**

(54) **METHOD AND DEVICE FOR PRODUCING FULLERENES**



(57) L'invention concerne un nouveau dispositif et un procédé pour la fabrication en continu de noirs de carbone à teneur élevée en fullerènes. Le dispositif comporte essentiellement un réacteur à plasma (1), un séparateur à chaud (2) situé en aval pour la séparation des constituants non volatils et un séparateur à froid (3) s'y raccordant.

(57) The invention relates to a method and a device for the continuous production of carbon black with a high fullerene content. The device essentially consists of a plasma reactor (1), a downstream heat separator (2) to separate the non-liquid constituents and a cold separator (3) attached thereto.



Yvan Schwob

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Method and Device for Producing Fullerenes

The invention relates to a method and a device for the continuous production of carbon black with a high fullerene content.

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In the following the term fullerenes refers to molecular, chemically homogenous and stable fullerenes. Representatives of this group of fullerenes are C_{60} , C_{70} or C_{84} . These fullerenes are generally soluble in aromatic solvents. A particularly preferred fullerene is the C_{60} fullerene.

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For the production of carbon black containing fullerenes several methods are known. However, the achievable concentration of fullerenes in the obtained carbon black is so low that a preparation of pure fullerenes is only possible with great expenditures. Due to the resulting high price of pure fullerenes interesting applications in different fields of technology are for economical reasons a priori not conceivable. The US-A 5,227,038 for example, discloses an apparatus for a laboratory allowing to produce a few grams of fullerenes in a discontinuous way by means of an electric arc between carbon electrodes serving as a raw material. Apart from the fact that the produced amounts are tiny, the concentration of fullerenes C_{60} in the deposited carbon black is very low and never exceeds 10 % of the produced mass. Further, the fullerene C_{60} is in this method present in a mixture with higher fullerene compounds requiring costly fractionation for an isolation with sufficient purity.

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The US-A 5,304,366 describes a method allowing a certain concentration of the product but using a system for filtering a gas circulation at a high temperature which is difficult to practically perform.

5 The EP-B1 0 682 561 describes a general method for the production of carbon black with a nanosstructure defined by the influence of a gascous plasma on carbon at high tcmperatures. In product series obtained in this way fullerenes may at sufficient treatment temperatures be obtained in a continuous technical way.

10 However, the reaction products resulting from the method according to EP-B1 0 682 561 are very impure and contain apart from carbon which has not been transformed into fullerenes at best 10 % fullerene C₆₀ as a mixture with higher fullerenes.

15 It was therefore the problem of the invention to develop a device and a method allowing to continuously produce carbon black with a high content of fullerenes. This problem was solved with the device according to the invention according to claim 1 and the method according to claim 12 based thereon.

20 **Description of the Figures:**

25 Figure 1: shows an embodiment of the device according to the invention, consisting essentially of a plasma reactor (1) with a first reaction chamber (A) and a second reaction chamber (B), a downstream heat separator and an attached cold separator (3).

Figure 2: shows a detail of the head part of the plasma reactor (1) comprising essentially the first reaction chamber (A).

30 Figure 3: shows a top view of the reactor (1) illustrating an embodiment of the invention with three electrodes (4) distributed with an angle of 120°, a

- 3 -

central supply device (5) for the carbon-containing material and a heat resistant and heat isolating lining.

5 Figure 4: shows a further embodiment of the device according to the invention consisting essentially of the same parts as figure 1, but wherein the flow of products in the plasma reactor (1) is directed opposite to gravity.

10 The device according to the invention consists according to claim 1 of the following components:

15 a) a plasma reactor (1) consisting of a first reaction chamber (A) into which two or more electrodes (4) are inserted; the first reaction chamber (A) further comprising a supply arrangement (5) for the plasma gas and the carbon-containing compounds delivering the plasma gas and the carbon-containing compounds centrally into the reaction zone; the plasma reactor (1) comprising a second reaction chamber (B) adjacent to the first reaction chamber (A) comprising suitable arrangements for cooling the reaction mixture exiting from the first reaction chamber (A),

20 b) a heat separator (2) attached to the plasma reactor, and

25 c) a cold separator (3) attached to the heat separator (2).

30 The plasma reactor (1) consists preferably of a cylindrically-shaped metal casing which may, if needed, be designed with a double wall. In this double wall a suitable cooling means may circulate. In the metal casing further an isolation (6) may be provided consisting generally of graphite or additionally of a ceramic

layer. The first reaction chamber (A) is only used for the plasma reaction at very high temperatures.

According to the invention two or more, preferably three electrodes (4) are inserted into the head part of the first reaction chamber (A). The electrodes are preferably arranged with an angle to the axis so that they form in the upper part of the first reaction chamber (A) an intersection and that they can individually and continuously be adjusted by conduit glands (7). The tilt with respect to the vertical axis is preferably in the range of 15° to 90°, however, in all cases the tilt is such that an easy start of the arc producing the plasma is possible and that a maximal stability of the plasma is assured.

Preferably, the electrodes (4) are equally distributed so that with three electrodes an angular distance of 120° results. Typically plasma electrodes are used which are common in the field of the experts. These electrodes consist typically of a graphite as pure as possible in the form of a cylindrical rod having generally a diameter of a few centimeters. If needed, the graphite may contain further elements having a stabilizing influence on the plasma.

The electrodes are generally operated with an alternating voltage between 50 and 500 volts. The applied power is typically in the range of 40 kW to 150 kW. A suitable control of the electrodes provides a constant and stable plasma zone. The electrodes are automatically readjusted corresponding to their consumption.

The supply device (5) serves as a feeding unit for the carbon-containing compounds as well as for the plasma gas. Devices allowing a constant supply common for an expert can be used to this end. The supply is preferably centrally into the plasma zone controlled by the electrodes. The second reaction chamber (B) comprises suitable devices for an effective and selective cooling of the reaction mixture exiting from the first reaction chamber (A). In a preferred embodiment a supply device (8) may be provided thereto allowing for example by

a cyclone effect a suitable distribution of, for example a plasma gas or, if needed, another cooling means.

According to the invention, the reaction mixture exiting from the second reaction 5 chamber (B) is delivered to a heat separator (2). The heat separator (2) is preferably designed in the form of an isolated or isothermally heated cyclone containing in the lower part a lock (9) for the separation of the non-volatile components, a conduit (10) for the recovery of the non-volatile components into the plasma reactor (10) and in the upper part a conduit (11) for leading the volatile 10 components into the cold separator (3). The isothermal heating of the cyclone can be achieved by common measures.

Alternatively, the heat separator may be replaced by a suitable heat-resistant filter. Such a filter can, for example, consist of heat-resisting materials and of a porous 15 ceramic, a metal frit or graphite foam. As in the case of the heat separator devices which are not shown, may allow a recovery of the separated solid compounds and lines may be provided for leading the gaseous compounds into the cold separator (3).

20 A cold separator (3) is connected to the heat separator (2) preferably in the form of a cyclone which can be cooled and which comprises in the lower part a lock (12) for the separation of the carbon black containing the fullerenes and in the upper part a conduit (10) for guiding the plasma gas back into the plasma reactor (1).

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The cooling of this cyclone may be carried out in a standard way, for example by means of a cooling jacket supplied with a cooling fluid.

In a further embodiment of the device according to the invention a conduit (13) 30 for the supplying of the cooling device of the second reaction chamber (B) may be branched off from the conduit (10).

Further, also an entry device (14) for the carbon-containing material may be present allowing to feed the carbon-containing material via a lock (15) into the conduit (10).

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A further subject of the invention is a method for the production of carbon black with a high content of the fullerenes mentioned at the beginning from carbon-containing compounds in a plasma by means of the above-described device according to the invention. The invention relates in particular to the production of 10 carbon black with a high content of C_{60} fullerenes.

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Preferably, the temperature of the plasma is adjusted so that the greatest volatility possible of the inserted carbon-containing material is achieved. Generally the minimum of the temperature in the first reaction chamber (A) is 4000 °C.

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As the plasma gas preferably a noble gas or a mixture of different noble gases is used. Preferably helium, if needed in a mixture with a different noble gas, is used. The used noble gases should be as pure as possible.

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As the carbon-containing material preferably a highly pure carbon is used which is as free as possible of interfering and the quality of the fullerenes negatively influencing impurities. Impurities as for example, hydrogen, oxygen or sulfur reduce the production yield of fullerenes and form undesired byproducts. On the other hand any gaseous impurity present in the circulation of the production cycle causes a decrease of the purity of the plasma gas and requires the supply of 25 plasma gas in a pure form to maintain the original composition. However, it is also possible to directly clean the plasma gas in the circulation of the production cycle. Preferably, highly pure, finely ground carbon powders e.g. acetylene black, graphite powders, carbon black, ground pyrolytic graphite or highly calcinated 30 coke or mixtures of the mentioned carbons are used. In order to obtain an optimal evaporation in the plasma, the mentioned carbon powders are preferably as fine as

possible. Coarser carbon particles may pass the plasma zone without being vaporized. In this case a device according to figure 4 may help wherein the carbon particles reach the plasma zone in the opposite direction with respect to gravity.

5 The carbon-containing material is preferably together with the plasma gas supplied via the supply arrangement (5) into the plasma reactor.

The plasma gas contains the carbon-containing material preferably in an amount of 0.1 kg/m^3 to 5 kg/m^3 .

10 The reaction mixture formed in the reaction chamber (A) is, as already mentioned above, with a sufficient efficiency cooled in the second reaction chamber (B) to keep it at a temperature of preferably between 1000°C and 2700°C for a defined time of generally fractions of a second up to a second. In this phase the gaseous 15 carbon molecules exiting from the first reaction chamber (A) recombine to the fullerenes mentioned at the beginning.

20 The cooling is achieved, as shown above, by suitable cooling devices, preferably by a homogenous distribution of a defined amount of cold plasma gas in the second reaction chamber (B). This cold plasma gas is preferably obtained from the recirculating plasma gas.

25 At the exit of the second reaction chamber (B) the mixture consists generally of the plasma gas, the desired fullerenes in a gaseous state, a fraction of the non-converted raw material and of non-vaporizable fullerenes.

In the heat separator (2), which is, as shown above, provided as a cyclone, the solid parts are separated from the gaseous parts by means of the cyclone effect.

The desired fullerene, which is volatile itself, can therefore with a yield of up to 90 % be separated from the other non-volatile carbon compounds.

5 The heat separator (2) is kept by known means isothermally on a temperature of preferably between 600 °C to 1000 °C to avoid any condensation of the desired fullerenes in any of their parts.

10 A lock (9) at the bottom of the heat separator (2) allows to lead the carbon which was not converted into the desired fullerene back into the gas circulation, for example by means of a blowing engine.

The above-mentioned but not in detail explained filter may fulfil the same function as the above-discussed heat separator (2).

15 A cold separator (3) follows the heat separator (2). This cold separator is by means of any known means cooled to a temperature sufficient for the condensation of the desired fullerene, preferable of a temperature ranging from room temperature up to 200 °C.

20 At the exit of the cold separator (3) generally a powder-like material accumulates containing carbon black with a fraction of the desired fullerenes of up to 40 %.

25 Thanks to the lock (12) the carbon black with the accumulated desired fullerenes may be taken from the process and be subjected to further purification. The further purification may be carried out in accordance with a known method, for example by extraction (Dresselhaus et al., Science of Fullerenes and Carbon

Nanotubes, Academic Press, 1996, Chapter 5, pp. 111, in particular Chapters 5.2 and 5.3).

5 The plasma gas coming from the cold separator (3) can be lead back, for example by means of a blowing machine, via the conduit (10) into the plasma reactor (1).

A branch (13) of this conduit (10) allows to guide a part of the cold flow back into the second reaction chamber (B) for cooling the reaction mixture.

10 The following examples illustrate the subject matter of the invention, however, without limiting it to the scope of the examples.

Examples:

15 **Example 1**

The device consists of a cylindrical reactor with an inner diameter of 300 mm, a height of 150 cm and a double-walled cooling jacket with water circulation. Between the graphite lining and the inner wall of the pressure chamber an isolating layer of graphite foam is arranged. Three graphite electrodes with a diameter of 20 mm are positioned with a sliding device through the reactor cover by means of conduit glands inserted into electrically isolating sockets. A central conduit with a diameter of 3 mm serves for introducing the graphite suspension into the plasmagenic gas. The plasma gas is pure helium kept in a circulation.

25 The electrodes are supplied with an alternating voltage such that the supplied power is 100 kW.

By a means of a three-phase controller of the type used in an arc furnace comparatively constant electrical properties on the plasma level are achieved. In this way a plasma temperature of approximately 5000 °C is kept in the reaction chamber (A).

5

The reaction chamber (B) is provided with cold gas guided back to keep its temperature on a value of approximately 1600 °C.

10 The raw material is micronized graphite of the type TIMREX® KS 6 of Timcal AG, CH-Sins. With an amount of gas of 10 m³/h on the height of the entrance of the reactor and a material addition of 10 kg/h, a permanent state is achieved after an operating time of 1 hour. In the heat separator (2), kept on a temperature of 800 °C, 8 kg/h of non-volatile carbon compounds were separated via the lock (9) and recovered. It was found that approximately 6 % of the introduced carbon was 15 under these conditions converted into the gaseous fullerene C₆₀. With an efficiency of the heat separator of approximately 90 % the fullerene C₆₀ was to a small extent mixed with non-volatile carbon compounds and helium. This aerosol was transmitted to the cold separator (3) kept on a temperature of 150 °C.

20 The product accumulating at the bottom of the cold separator (3) was during constant operation removed from the lock (12) in an amount of 2 kg/h and consisted of 30 % fullerene C₆₀ as a mixture with non-converted carbon.

25 The obtained product can in this state be used, however it was further purified according to Dresselhaus et al., Science of Fullerenes and Carbon Nanotubes, Academic Press, 1996, Chapter 5, pp. 111, in particular Chapters 5.2 and 5.3, by extraction with toluol. The exemplary production allows the production of 0.6 kg/h of pure fullerene C₆₀.

Example 2

5 The method according to example 1 was repeated, only helium was replaced by argon. Under these conditions pure fullerene C₆₀ could be obtained after purification in the amount of 0.4 kg/h.

Example 3

10 The method according to example 1 was repeated, only the heat separator (2) was replaced by a filter of porous ceramic. The gas flow coming from the filter and entering the cold separator (3) consisted only of helium mixed with gaseous fullerene C₆₀. The efficiency of the filter was approximately 90 %. According to this method pure fullerene C₆₀ could be obtained after purification with an amount of 0.6 kg/h.

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Example 4

20 A method according to example 1 was repeated, only the micronized graphite was replaced by a highly pure acetylene black of the company SN2A, F-Berre l'Etang. With this method pure fullerene C₆₀ with an amount of 0.8 kg/h could be obtained after purification.

Example 5

25 The method according to example 1 was repeated, only the micronized graphite was replaced by a highly pure, degassed pyrolytic graphite of the type ENSACO Super P of the company MMM-Carbon, B-Brussels. With this method pure fullerene C₆₀ with an amount of 0.7 kg/h could be obtained after purification.

Claims

1. Device for the continuous production of carbon black with a high content of fullerenes from carbon-containing compounds in a plasma consisting of
 - 5 a) a plasma reactor (1) consisting of a first reaction chamber (A) in which two or more electrodes (4) are inserted, wherein the first reaction chamber (A) further includes a supply arrangement (5) for the plasma gas and the carbon-containing compounds to lead the plasma gas and the carbon-containing compounds centrally into the reaction zone, wherein the plasma reactor (1) includes a second reaction chamber (B) adjacent to the first reaction chamber (A) having suitable devices for cooling the reaction mixture exiting from the first reaction chamber (A),
 - 10 b) a heat separator (2) attached to the plasma reactor (1) and
 - 15 c) a cold separator (3) attached to the heat separator (2).
2. Device according to claim 1, characterized in that the plasma reactor (1) is provided with a heat-resistant and heat-isolating lining (6).
- 20 3. Device according to claim 2, characterized in that the lining (6) consists of graphite.
4. Device according to one of the claims 1 to 3, characterized in that the two or more electrodes (4) are arranged with an angle to the axis in such a way that they form in the upper part of the first reaction chamber (A) an intersection and that they are individually adjustable in the direction of

their axis by means of conduit glands (7) inserted into the reaction chamber.

5. Device according to claim 4, characterized in that three electrodes (4) are used, which are operated with a three-phase-alternating voltage and consist of graphite.
6. Device according to one of the claims 1 to 5, characterized in that a supply arrangement (8) for plasma gas is provided as a device for cooling.
- 10 7. Device according to one of the claims 1 to 6, characterized in that the heat separator (2) is provided in the form of an isothermally heatable cyclone, comprising in the lower part a lock (9) for the separation of the non-volatile compounds and a conduit (10) for guiding the non-volatile compounds back into the plasma reactor (1) and a conduit (11) in the upper part for guiding the volatile compounds into the cold separator (3).
- 15 8. Device according to one of the claims 1 to 7, characterized in that the heat separator (2) is provided in the form of a heat-resistant filter.
- 20 9. Device according to one of the claims 1 to 8, characterized in that the cold separator (3) is provided in the form of a cyclone which can be cooled, including in the lower part a lock (12) for the separation of the carbon black containing the fullerenes and in the upper part a conduit (10) for guiding the plasma gas back into the plasma reactor (1).
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10. Device according to claim 9, characterized in that a conduit (13) which is provided as a supply of the plasma gas into the second reaction chamber (B) branches off from the conduit (10) provided for guiding the plasma gas back into the plasma reactor.

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11. Device according to one of the claims 1 to 10, characterized in that an entry device (14) for the carbon-containing material is present, allowing to feed the carbon-containing material via a lock (15) into the conduit (10).

10 12. Method for the continuous production of carbon black with a high content of fullerenes characterized in that carbon-containing compounds in the plasma are converted by means of a device according to one of the claims 1 to 11.

15 13. Method according to claim 12 characterized in that chemically homogenous stable fullerenes are produced.

14. Method according to claim 12 or 13 characterized in that the fullerene C₆₀, C₇₀ or C₈₄ or mixtures of these fullerenes are produced.

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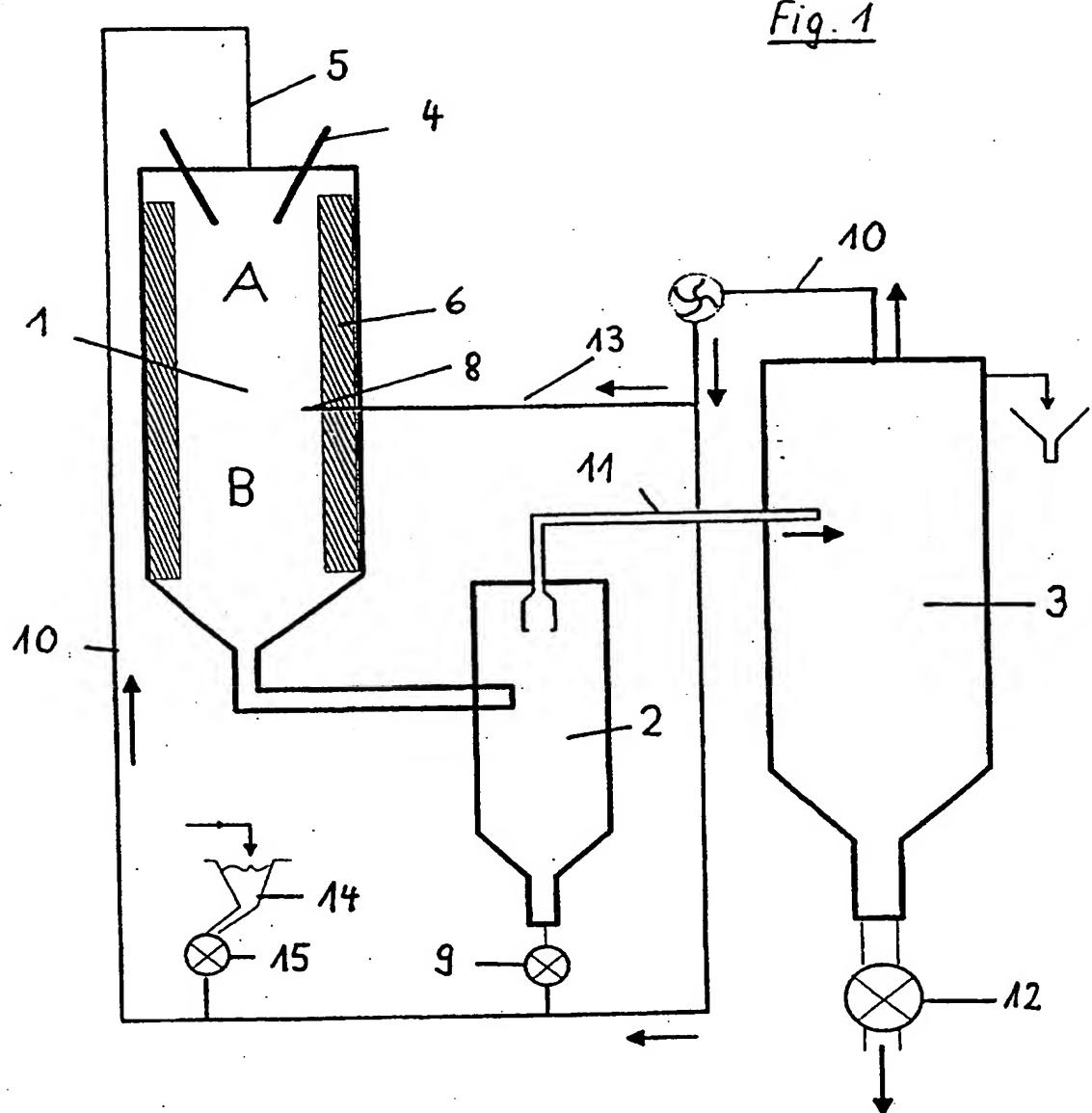
15. Method according to one of the claims 12 to 14 characterized in that the plasma temperature has a minimal temperature of 4000 °C in the first reaction chamber (A).

25 16. Method according to one of the claims 12 to 15 characterized in that a noble gas or a mixture of different noble gases is used as the plasma gas.

17. Method according to one of the claims 12 to 16 characterized in that helium is used as a plasma gas.
18. Method according to one of the claims 12 to 17 characterized in that a highly pure carbon e.g. acetylene black, graphite powder, carbon black, ground pyrolytic graphite or highly calcinated coke or mixtures of the mentioned carbons are used as the carbon-containing material.
19. Method according to one of the claims 12 to 18 characterized in that the temperature in the second reaction chamber (B) is kept at a temperature between 1000 °C to 2700 °C.
20. Method according to claim 19 characterized in that the temperature in the second reaction chamber (B) is regulated by the supply of cool plasma gas from the supply device (8).
21. Method according to one of the claims 12 to 20 characterized in that the heat separator (2) is isothermally kept at a temperature of 600 °C to 1000 °C.
22. Method according to one of the claims 12 to 21 characterized in that the cold separator (3) is operated at a temperature ranging from room temperature to 200 °C.
23. Method according to one of the claims 12 to 22 characterized in that a carbon black with a high content of C₆₀ fullerenes is produced.

Abstract

5 The invention relates to a method and a device for the continuous production of carbon black with a high fullerene content. The device essentially consists of a plasma reactor (1), a downstream heat separator (2) to separate the non-volatile constituents and a cold separator (3) attached thereto.



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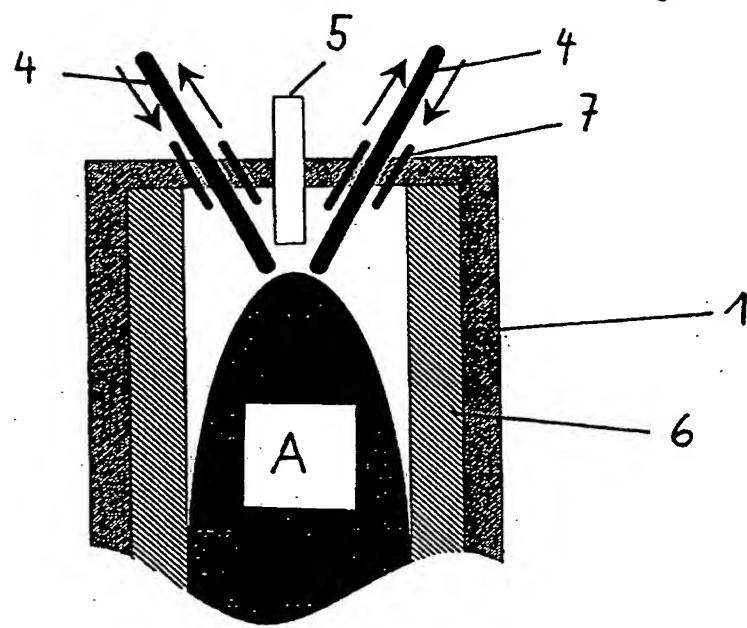
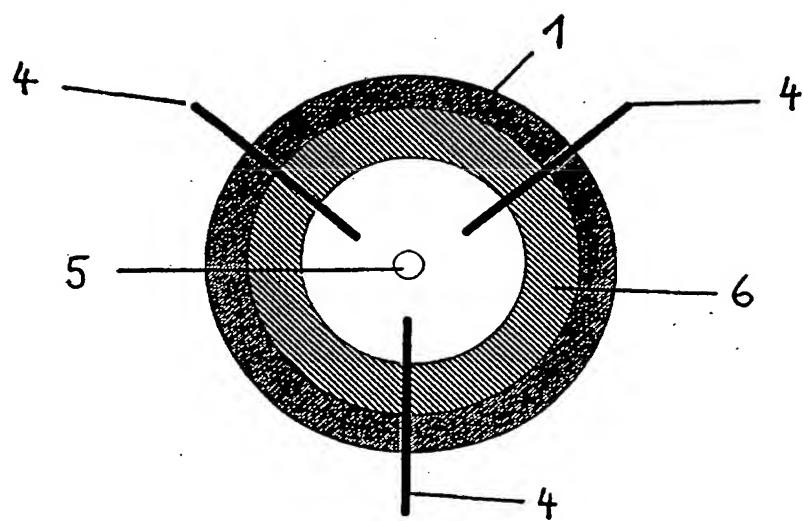
Fig. 2Fig. 3

Fig. 4